First-principles investigation of terephthalic acid on Cu(110)

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(Received 7 February 2007; published 25 September 2007)

We performed first-principles calculations within the density functional theory aimed to investigate the two-dimensional geometry of one monolayer of terephthalic acid (TPA) adsorbed on Cu(110) surface. The key issue of our study is to elucidate if the molecule-molecule interactions include a hydrogen bond, since such a bond would hinder the possibility to chemically functionalize this surface [see D. S. Martin *et al.*, Phys. Rev. B **66**, 155427 (2002)]. In this context, our *ab initio* simulations are focused on the role of the spatial position of the hydrogen atom of the carboxylic group (COOH) for the structural stability of the TPA-Cu(110) system. It was found that an adsorption geometry involving a hydrogen bond is energetically unfavorable. The energy barrier separating these configurations was calculated for several different pathways of rotating the H—O bond of the carboxylate group (OCO). We also analyze the real-space topography of four different adsorption geometries by simulating scanning tunneling microscopy (STM) images for several values of the applied bias voltage (±0.5, ±1, and ±2 eV). At small positive bias voltage (±0.5), only two adsorption configurations can be imaged by STM. Besides this, theoretical STM images of these structures show specific feature for each case considered, and thus they can help to experimentally discriminate between the TPA-Cu(110) geometries considered in our study.

DOI: 10.1103/PhysRevB.76.115433 PACS number(s): 71.15.Mb, 68.43.−h, 68.37.Ef

I. INTRODUCTION

The development of technologies based on molecular organic semiconductor materials has been proven to lead to reliable devices such as organic light-emitting diodes[1,2] commonly used in flat display industry. To circumvent the limits of a silicon-based microchip technology, special attention was focused on the development of electronic devices based on organic molecules. This effort has triggered the development of the molecular electronics field (see, for instance, Refs. 3–5), and promising experiments aimed to design single molecule diodes[6–8] or thin-film transistors[9] have already been performed.

A very popular approach to construct such molecular electronic devices is to choose molecules that possess specific electronic properties and try to attach them between metallic or semiconductor leads. The practical success of this approach relies on the hope that after adsorption, the specific molecular properties will remain or that properties with possible technological applications will be induced in the adsorbed molecules or at the molecule-substrate interface.

A much more systematic approach to construct reliable molecular electronic devices is to develop methods to *selectively* change the functionality of specific molecules adsorbed on surfaces. In this case, one can use molecules that have several functional groups such that one of them can be utilized to anchor the molecules at the surface. The other functional groups are employed to modify *in situ* the molecular structure by reacting it with other specific molecules by means of well-known chemical reactions and so to induce the desired electronic properties in the molecular electronic device.

The development of such organic-metal interfaces is therefore essential in the field of nanotechnology, since it allows us to tune the properties of the adsorbate-substrate system according to desired technological needs. Besides the impact on the molecular electronics field, a functionalized organic-metal interface has important applications such as lithography[10,11] and molecular recognition.[12]

Despite this large technological interest, the interaction of organic molecules with metallic surfaces is still a matter of debate. Recent insight on this issue was gained by means of *ab initio* calculations.[13–17] A central topic of these studies is the understanding of the bonding mechanism of the organic molecules on metallic substrates as well as the two-dimensional structure of the molecular layer. Even if the specific details of molecule-substrate interaction depend on the physical system under consideration, the general picture emerging from these theoretical studies is that the binding and ordering of molecules on the metallic surfaces are the result of a competition between the adsorbate-substrate and adsorbate-adsorbate interactions.

Recently, the practical possibility to chemically functionalize the Cu(110) surface upon adsorption of terephthalic acid (TPA) was experimentally investigated by means of low-energy electron diffraction (LEED), temperature programed desorption, reflection anisotropy spectroscopy (RAS), and reflection absorption infrared spectroscopy.[18] In this study, it was shown that the TPA adsorbs to the Cu(110) surface as monocarboxylate species following deprotonation of an acid group. At low coverage, the molecule adopts a flat-lying adsorption geometry, while increasing the coverage leads to a reorientation of the adsorbed species toward the surface normal (upright adsorption geometry). The latter case is of particular interest in the context of the surface functionalization process, since only in this case the second carboxylic group of TPA is located at the vacuum interface [see Fig. 2(a)] and thus a substitution of the hydrogen or hydroxyl group (OH) by other organic molecules becomes possible.

In the case of high coverage, the TPA adsorbs with the oxygen atoms on top of copper ones in a densely packed

$p(2\times1)$ phase, a coverage which has been observed for the 3-thiophene carboxylate/Cu(110) system.[19] The bonding mechanism is similar to that evidenced for the adsorption of several monocarboxylic acids on Cu(110) surface.[20–24] However, less information is known about the two-dimensional order induced by molecule-molecule interactions. In particular, it is not clear if a dimerization process involving the adsorbed TPA molecules takes place in this case. This is a critical aspect since a hydrogen bond between the TPA molecules adsorbed on Cu(110) surface would possibly hinder the functionalization of this surface.[18] Therefore, the basic goal of the present paper is to elucidate the two-dimensional order of one TPA monolayer adsorbed on Cu(110) surface with a special emphasis on the geometrical structure of the carboxylic group. To reach this aim, we performed extensive *ab initio* total-energy calculations for several molecular configurations with different atomic positions of the carboxylic hydrogen atom. Our simulations show that the structure without a hydrogen bond [see Fig. 2(a)] is energetically more stable than that which would present such a bond. More precisely, a dimerized TPA-Cu(110) configuration with a hydrogen bond is structurally unstable and it relaxes to the geometry depicted in Fig. 2(c). This adsorption configuration also allows a chemical functionalization of the Cu(110) surface, and thus we investigated if a structural transition between geometries with different orientation of the H—O bond is possible. Since a practical way to distinguish between different metallic surface structures is to analyze their real-space topography as provided by scanning tunneling microscopy (STM), for each configuration under consideration, we simulated the corresponding STM images. The simulated images exhibit peculiar features for each case considered, and thus it is possible to unambiguously identify in experiments which specific TPA-Cu(110) geometry is investigated.

II. THEORETICAL METHOD

Our study is performed within the framework of density functional theory[25] employing the generalized gradient approximation for exchange-correlation energy functional.[26] The Kohn-Sham equations[27] have been solved self-consistently using the pseudopotential method[28] as implemented in the ESTCOMPP program.[29,30] In this code, the electron-ion interactions are replaced by norm-conserving pseudopotentials generated according to the scheme proposed by Bachelet *et al.*[31] in the Kleinman-Bylander form[32] or by non-norm-conserving pseudopotentials as described by projector augmented-wave method (PAW).[33] In the present work, we used for H atom its bare Coulomb potential, while for C, O, and Cu atoms, we employed PAW-like pseudopotentials. The technical details regarding the parameters used to generate these pseudopotentials are described in Refs. 24 and 34.

The Cu(110)-(2×1) surface was modeled by a periodic slab geometry. In each supercell, the slab consists of seven atomic layers with two Cu atoms in each layer. The thickness of the vacuum region separating the slabs along the direction perpendicular to surface is about 26.5 Å. At each side of the slab, one TPA molecule was adsorbed. The geometry of the TPA-Cu(110) system was optimized by relaxing the atomic positions of all atoms belonging to two TPA molecules and those in two surface layers at each side of the slab. The equilibrium geometry of the TPA-Cu(110) system was obtained by imposing an accuracy of the calculated Hellmann-Feynman forces better than 1 mRy/a.u.. The Kohn-Sham orbitals were expanded over a plane-wave basis set which includes all plane waves up to a cutoff energy E_{cut} of 25.0 Ry. With this choice, the theoretical lattice parameter of the bulk Cu is 3.642 Å, which is about 1% larger than the experimental value of 3.61 Å. The Brillouin zone integrations were replaced by a sum over a $3\times4\times1$ Monkhorst-Pack[35] **k** mesh.

A key goal of our study is to investigate the structural stability of different conformational geometries of the adsorbate-surface system in the limit of a high coverage. In order to perform such an analysis, we calculated the adsorption energy E_{ads} and adsorption enthalpy $\Delta H^{ads}_{T=0}$ at a temperature T of 0 K for each geometry under consideration.

The adsorption energy E_{ads} is generally defined as $E_{ads}=E_{sys}-E_{\mathrm{Cu}(110)}-E_{MTP}$, where E_{sys} represents the total energy of the adsorbed TPA-Cu(110) surface system while $E_{\mathrm{Cu}(110)}$ and E_{MTP} are the total energies of the isolated Cu(110) surface and isolated deprotonated TPA molecule (i.e., a monoterephtalate functionality), respectively. Since in our total-energy calculations we employed a symmetric slab with one deprotonated TPA molecule adsorbed on each side of slab, the adsorption energy E_{ads} per TPA molecule is given by

$$E_{ads}=\frac{1}{2}[\,E_{sys}-E_{\mathrm{Cu}(110)}-2E_{MTP})], \tag{1}$$

where a factor of 1/2 accounts for the fact that our slab contains two identical surfaces.

The adsorption enthalpy $\Delta H^{ads}_{T=0}$ is defined as the difference between the sum of the product energies (E_{sys} and E_{H_2}) and the sum of reactant energies ($E_{\mathrm{Cu}(110)}$ and E_{TPA}). Here, E_{H_2} stands for the total energy of the isolated hydrogen molecule H_2 and E_{TPA} is the total energy of the isolated TPA molecule. In a similar way to Eq. (1), for our specific slab geometry, the $\Delta H^{ads}_{T=0}$ per TPA molecule is given by

$$\Delta H^{ads}_{T=0}=\frac{1}{2}[(E_{sys}+E_{\mathrm{H}_2})-(E_{\mathrm{Cu}(110)}+2E_{TPA})]. \tag{2}$$

A negative adsorption enthalpy indicates an exothermic reaction between the TPA molecule and the Cu(110) surface, while a positive value of $\Delta H^{ads}_{T=0}$ implies that such reaction is endothermic and requires external energy to make it possible.

III. RESULTS

A. Isolated terephthalic acid molecule

The terephthalic acid crystallizes in a centrosymmetric monoclinic structure with two crystalline modifications[36] or in a monoclinic system.[37] Regardless of the crystalline structure, the TPA molecules arrange themselves in infinite chains via weak hydrogen bonds.

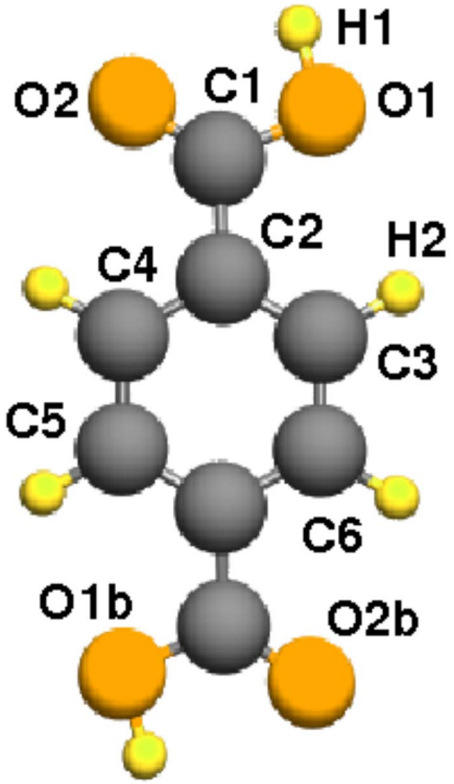

FIG. 1. (Color online) Color of atoms: C, dark gray; O, orange (gray); H, yellow (light gray). Ball-and-stick model of the isolated terephthalic acid (TPA) molecule with the numbering of the atoms referred to in the text.

To deposit TPA molecules on Cu(110) surface, the crystalline TPA was sublimated in special ultrahigh vacuum conditions.[18] Therefore, we optimized the geometrical structure of the TPA molecule in the gas phase using a C_i point group symmetry employed also in our slab calculations. This structural optimization was carried out by placing one TPA molecule (see Fig. 1) in an orthorhombic supercell with dimensions $12.0\times7.5\times17.0$ Å^3. The calculated bond lengths and bond angles are reported in Table I.

Since there are no experimental structural data for the TPA molecule in gas phase, we compare our computed bond lengths and angles with those obtained from x-ray measurements performed for crystalline triclinic (form I)[36] and crystalline monoclinic[37] terephthalic acid. On average, theoretical bond distances of the isolated TPA molecule are slightly larger than their counterparts in solids. This general feature is the result of the fact that in crystals the hydrogen atoms are shared between the carboxylate groups of the neighboring molecules to form van der Waals crystalline solids. The average C—C bond distance is about 1.429 Å, which closely resembles the C—C bond length in graphite (1.42 Å). Besides this, one can observe that for an isolated molecule as well as for crystalline TPA, the benzene ring (C_6H_4) is slightly distorted from an ideal hexagonal geometry. However, the overall geometry of the TPA molecule is closely planar in all cases mentioned here.

TABLE I. The bond lengths and bond angles calculated (a) for the TPA molecule in gas phase and (b) for TPA adsorbed on Cu(110) surface. The atomic labels are indicated in Fig. 1.

	This work			
	(a)	(b)	Ref. 36	Ref. 37
	Bond length (Å)			
C1-O1	1.390	1.387	1.272	1.248
C1-O2	1.291	1.281	1.262	1.248
C1-C2	1.480	1.480	1.483	1.493
C2-C3	1.417	1.412	1.406	1.369
C2-C4	1.415	1.410	1.401	1.369
C4-C5	1.405	1.399	1.370	1.384
Cu-O1b		1.949		
Cu-O2b		1.952		
	Bond angle (deg)			
O1-C1-O2	121.7	124.0	123.5	122.4
O1-C1-C2	113.6	109.8	117.0	118.8
O2-C1-C2	124.7	126.2	119.5	118.8
C1-C2-C3	122.4	119.4	120.2	120.1
C1-C2-C4	122.4	121.0	119.4	120.1
C3-C2-C4	119.3	119.6	120.4	119.9
C2-C4-C5	120.4	119.8	119.4	120.1
C2-C3-C6	120.3	120.6	120.2	120.1

B. TPA-Cu(110) system

Atomic structure. In the following, we will focus on the analysis of the lateral interactions between TPA molecules absorbed on Cu(110) surface in the limit of high coverage. As depicted in Fig. 2(a), in the case of high coverage, one terephthalic TPA molecule is adsorbed in an upright configuration on a (2×1) surface unit cell of the Cu(110) surface.

As mentioned in the Introduction, the adsorption process of TPA on Cu(110) surface as a function of molecular coverage was experimentally investigated by means of reflection absorption infrared spectroscopy (RAIS), LEED, and RAS.[18] In this study, it was shown that for a low coverage, the adsorbed molecules adopted a flat-lying geometry on Cu(110) surface, while for a saturated monolayer (high coverage), they orient perpendicular to surface. In the latter case, the TPA deprotonates leading to the formation of one carboxylate group (OCO), and the binding of TPA to Cu(110) surface is realized through the carboxylate group in the so-called bridge configuration along the $[1\bar{1}0]$ direction with O atoms located on top of Cu ones [see Fig. 2(a)]. The peculiar feature of this adsorption geometry is that the O atoms form one single bond with Cu ones. A similar bonding mechanism was evidenced for the high-coverage adsorption of 3-thiophene on Cu(110) surface.[20] Similarly, the stability of this bridge configuration compared to other possible adsorption geometries was recently obtained by first-principles calculations aimed to investigate the adsorption mechanism of formate on Cu(110) surface.[24,34]

The strength of the Cu—O chemical bonds can be qualitatively assessed from the length of the Cu—O bond. As

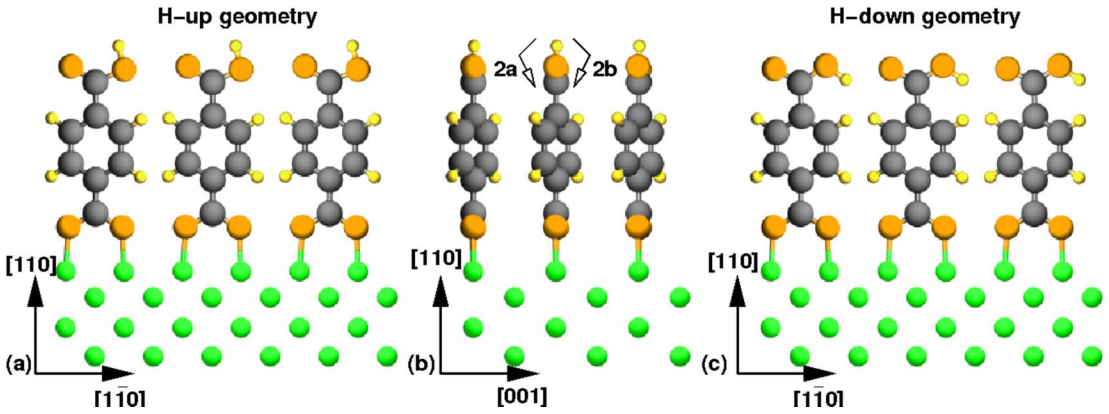

FIG. 2. (Color online) Color of atoms: Cu, green (gray, small spheres); C, dark gray; O, orange (gray, large spheres); H, yellow (light gray). Ball-and-stick model of the TPA adsorbed on Cu(110) surface. In this figure, we show the upper part of the slab consisting of two bulk Cu layers and two surface layers together with a terephthalate molecule in the surface unit cell. Along the [001] and [1$\bar{1}$0] directions, three unit cells are represented. (a) At high coverage, the TPA molecule adsorbs with an upright orientation with the carboxylate groups (COO) aligned along [1$\bar{1}$0] direction. In the adsorption configuration with lowest energy, the H atom of the carboxylic group (COOH) is pointing toward the vacuum (H-up geometry). (b) The lateral interactions between adjacent TPA molecules induce a rotation of the benzene ring (C_6H_4) with respect to the carboxylate plane by an angle of 24.7°. The 2a and 2b paths describe two possible ways to rotate H—O bond around the C—O one (see text). (c) Starting from a configuration with a hydrogen bond between two adjacent TPA molecules, the relaxed geometry is characterized by an H—O bond in the plane of the carboxylic group pointing toward the benzene ring (H-down geometry).

reported in Table I, the average Cu—O bond length is about 1.950 Å, which agrees well with that calculated for formate-Cu(110) system (1.994 Å) (Refs. 24 and 34) and with those obtained for adsorbed tartaric acid isomers on the same surface (1.97–1.99 Å).[22] A short Cu—O bond distance as revealed by our calculations is a sign of a strong Cu—O attractive interaction.[22] A strong Cu—O interaction is also apparent from a larger O—C—O bond angle of the adsorbed molecule compared to the gas phase (126.6° and 121.7°, respectively).

Another aspect investigated in our theoretical study concerns the relaxation of the Cu(110) surface in the presence of the adsorbate. The net effect of the terephthalate monolayer on the geometry of substrate is a very small outward relaxation of Cu atoms in the first layer while all other surface atoms keep their ideal surface positions. A similar trend was observed for the formate-Cu(110) system.[24,34]

From Table I, one can also observe that the C—C bond lengths are almost the same as those calculated for the isolated TPA molecule. However, in order to minimize the interaction between the hydrogen atoms which belong to neighboring benzene groups, the benzene rings rotate with respect to carboxylate groups. The angle between the normals to benzene ring corresponding to isolated and adsorbed TPA molecules is about 24.7°. No experimental data are available for this quantity even if it was speculated on the basis of steric considerations that such rotation should occur.[18] However, this effect was experimentally observed in scanning tunneling microscopy images recorded for 3-thiophene carboxylate on Cu(110) surface.[20]

So far, we described the geometry of adsorbate-substrate system depicted in Fig. 2(a). In this configuration, the hydrogen atoms of the acid group (COOH) are located on top of oxygen ones (the "H-up" geometry with a C—O—H bond angle of 101.2°). Another possible configuration would correspond to a hydrogen bond between adjacent adsorbed molecules. This possible geometry was mentioned by Martin *et al.* in Ref. 18; however, their RAIS data failed to evidence such a bonding interaction. Our *ab initio* simulations showed that a dimerized TPA-Cu(110) geometry with a hydrogen bond always relaxes toward the adsorption structure depicted in Fig. 2(c) (the "H-down" configuration with a C—O—H bond angle of 248.7°). It is important to note that *both* adsorption configurations can be employed as a starting point to chemically functionalize the Cu(110) substrate. However, it is important to note that the H-down configuration provides a more efficient starting point in this functionalization process than the H-up geometry. The basic reason is that a chemical reaction at the vacuum interface requires the presence of free orbitals spatially localized at this interface. In our case, the oxygen atom of the hydroxyl group H1-O1 (see Fig. 1) exhibits in all studied configurations an sp^3 hybridization. In the case of the H-up configuration, one of these orbitals is used for the binding to H1, and thus the hydrogen atom will probably hinder the chemical reactions which can take place at the oxygen. On the contrary, for the H-down geometry, the oxygen O1 atom has two sp^3-like orbitals at the vacuum interface and thus a chemical reaction can easily take place in this case (see Appendix).

Energetics. From a practical point of view, it is important to know which adsorption geometry is more likely to occur during an experiment. In order to answer this question, we compared the adsorption energies E_{ads} and adsorption enthalpies $\Delta H^{ads}_{T=0}$ calculated for the H-up and H-down configurations. From Table II, one can infer that the H-up geometry is lower in total energy than the H-down one, although the energy difference between these configurations is quite small ($\approx$0.08 eV). Furthermore, we considered two additional H-up and H-down geometries where the carboxylic group was aligned parallel to the benzene ring. These configura-

TABLE II. The adsorption energies E_{ads} and adsorption enthalpies $\Delta H^{ads}_{T=0}$ per TPA molecule calculated for the H-up and H-down geometries [see Figs. 2(a) and 2(e), respectively]. The H-up and H-down parallel configurations correspond the case when the carboxylic group (COOH) is in the same plane as benzene ring (C_6H_4).

Configuration	Adsorption energy E_{ads} (eV)	Adsorption enthalpy $\Delta H^{ads}_{T=0}$ (eV)
H-up	−3.0857	−0.6548
H-up parallel	−2.6961	−0.2651
H-down	−3.0047	−0.5738
H-down parallel	−3.0026	−0.5716

tions, denoted by H-up parallel and H-down parallel, are even higher in energy than the H-down one. However, one can observe from Table II that the three adsorption geometries (H-up, H-down, and H-down parallel) are very close in energy. This observation raises the question if a transition between the H-up and H-down (H-down parallel) configurations is energetically possible.

In order to check if such scenario is possible, we calculated the energy barrier corresponding to a rotation of the hydrogen atom from the H-up configuration to the H-down one. Two different paths have been considered: one in which the H—O bond was rotated in the plane of the carboxylate group (denoted as path 1) and one in which the H—O bond was rotated around the C—O bond of the carboxylate group. In the latter case, one can further distinguish between a clockwise and a counterclockwise rotation denoted by path 2a and 2b, respectively [see Fig. 2(b)]. The potential energy profiles corresponding to these paths are depicted in Fig. 3. One can observe that the rotation of the H—O bond in the plane of the carboxylic group (path 1) leads to a higher energy barrier (1.42 eV) than those involved in paths 2a and 2b

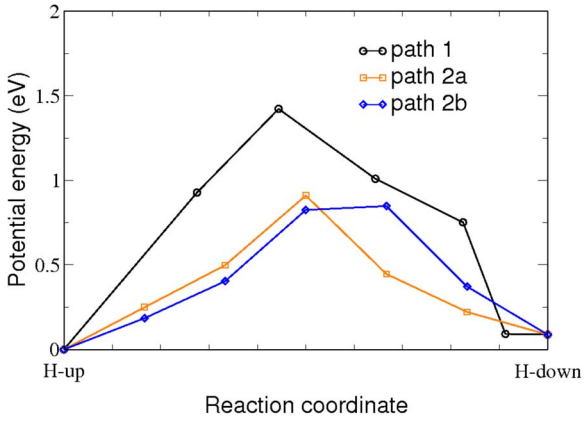

FIG. 3. (Color online) Potential energy barriers separating the H-up and H-down geometries (see Fig. 2). The rotation of the H—O bond in the plane of the carboxylic group (path 1, the black line) leads to a barrier height of 1.42 eV, while the rotations around the C—O bond give heights of 0.91 and 0.85 eV [path 2a, the red (dark gray) line, and path 2b, the green (light gray) line, respectively].

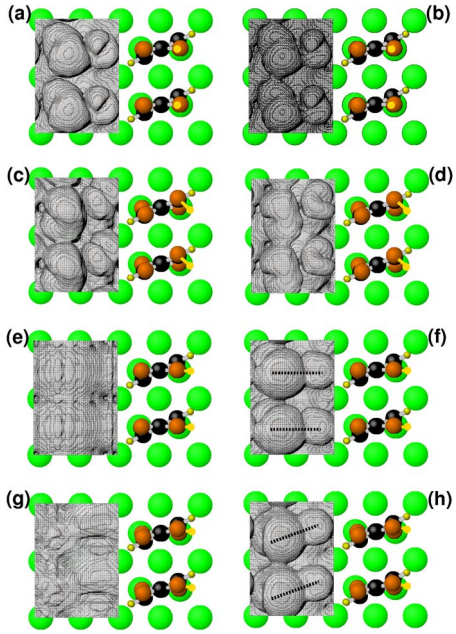

FIG. 4. (Color online) Color of atoms: Cu, green (gray, large spheres); C, black; O, orange (dark gray, small spheres); H, yellow (light gray). The calculated constant-current STM images of one TPA monolayer chemisorbed on Cu(110) surface for an applied bias voltage of ±0.5 eV. On the left, the STM images correspond to the occupied states while those on the right describe the unoccupied ones. Four different adsorption geometries have been considered: H-up [(a) and (b)], H-up parallel [(c) and (d)], H-down [(e) and (f)], and H-down parallel [(g) and (h)].

(0.91 and 0.85 eV, respectively). Another observation concerns the shape and height of the potential energy along paths 2a and 2b, which are slightly different. This difference is due to the fact that on path 2a, the hydrogen atom which belongs to carboxylic group closely approaches a hydrogen atom of the benzene ring, while the distance between these hydrogen atoms remains larger on path 2b.

Since the total-energy difference between the H-up and H-down geometries is quite comparable with thermal energy at room temperature (k_BT=0.026 eV), the question is if in this case the hydrogen atom can fluctuate between these configurations. Depending on the prefactor Γ_0 for the reaction rate $\Gamma=\Gamma_0 \exp(-E_a/kT)$, we can expect a transition rate at room temperature of 0.1 s^{-1} (for $\Gamma_0=10^{13}$) and 10^{-4} s^{-1} (for $\Gamma_0=10^{10}$) for the low activation energy of 0.85 eV. However, at slightly larger temperatures, a transition rate of 1 s^{-1} can be obtained.

To resume, our first-principles simulations showed that there is no dimerization between TPA molecules adsorbed on the Cu(110) surface due to hydrogen bonding interactions. A direct consequence of this fact is that the acid group can be used to chemically functionalize this surface. However, depending on the position of its hydrogen atom, this acid group can accommodate different functional groups and thus can allow a *specific* chemical functionalization of Cu(110) surface. Even if the room temperature thermal fluctuations between configurations with different H—O bond orientations is small, we suppose that such a process can be accelerated by applying a voltage via an STM tip.

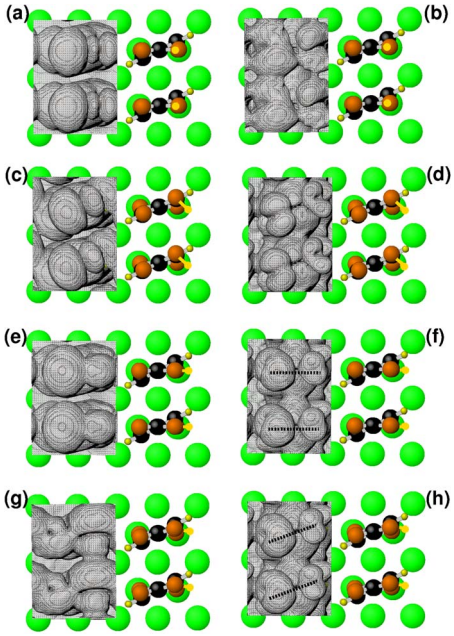

FIG. 5. (Color online) Color of atoms: Cu, green (gray, large spheres); C, black; O, orange (dark gray, small spheres); H, yellow (light gray). The simulated constant-current STM images of one TPA monolayer chemisorbed on Cu(110) surface for an applied bias voltage of ±1.0 eV. The order of the STM images is the same as in Fig. 4.

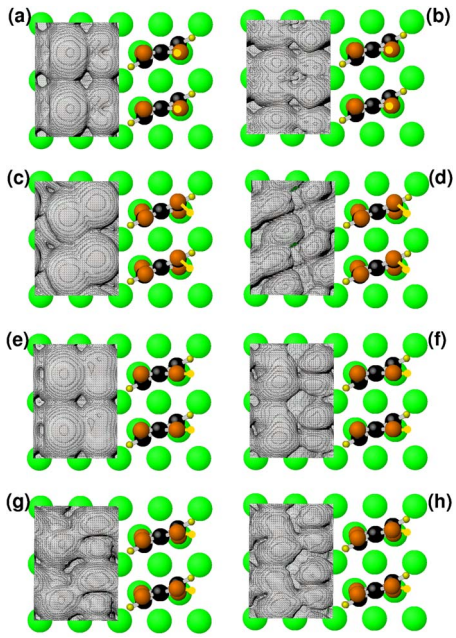

FIG. 6. (Color online) Color of atoms: Cu, green (gray, large spheres); C, black; O, orange (dark gray, small spheres); H, yellow (light gray). The calculated constant-current STM images of one TPA monolayer chemisorbed on Cu(110) surface for an applied bias voltage of ±2.0 eV. The order of the STM images is the same as in Fig. 4.

Electronic properties. A very powerful experimental method to distinguish between various conformations of molecules adsorbed on metallic surfaces is represented by scanning tunneling microscopy (STM). Despite the crucial importance of the details of the adsorption geometry of TPA on Cu(110) surface on its chemical functionalization, no experimental STM data are available for this physical system. Therefore, we simulated the STM images for all four different adsorption geometries considered in our study using the Tersoff-Hamann theory.[38]

The calculated constant-current STM images of one TPA monolayer chemisorbed on Cu(110) surface are presented in Figs. 4–6 for an applied bias voltage of ±0.5, ±1.0 and ±2.0 eV, respectively. In general, the specific features of the simulated STM images (i.e., the positions of maxima and minima) are particular for each adsorption geometry at each value of the bias voltage. Besides this, these theoretical images also exhibit a different topography depending if one probes the occupied or unoccupied states.

For instance, let us focus on the STM images obtained for an applied bias voltage of ±0.5 V. One can clearly observe that the STM images simulated for H-up [see Fig. 4(a)] and H-up parallel [see Fig. 4(c)] geometries look very similar except for the orientation of a small peak associated with a H—O bond oriented toward the vacuum interface. This peculiar feature of the simulated STM images is valid for both occupied and unoccupied states. Similarly, the calculated STM images for H-down and H-down parallel geometries [see Figs. 4(f) and 4(h), respectively] show a specific peak whose position depends on the orientation of the carboxylic group with respect to that of the benzene ring. However, this is the case only for STM images simulated for the unoccupied states that show specific features, while those obtained for the occupied ones [see Figs. 4(e) and 4(g), respectively] are featureless. One should emphasize that this particular behavior is observed *only* for the STM images obtained at this bias voltage. By increasing the applied bias voltage, the correspondence between the topography of the simulated STM images and the geometrical structure of the adsorbate-Cu(110) surface becomes less intuitive. This is exactly the reason why our theoretical STM images will provide a necessary support to interpret the experimental STM images obtained for various possible configurations of TPA-Cu(110) system.

A qualitative evaluation of the differences of the simulated STM images for the different configurations can be derived from the comparison of the total density of states (TDOS) reported in Fig. 7. The basic observation inferred from the calculated TDOS is that the STM images should exhibit larger differences for the considered adsorption geometries when imaging the occupied states compared to the unoccupied ones. By tuning the bias voltage to the characteristic peaks of the TDOS or by scanning tunneling spectroscopy, the differentiation between the configurations could be appreciably enhanced. Indeed, the average value of the constant LDOS used to simulate the STM images of the occupied states is $\approx 10^{-9}$, while for the unoccupied ones the value is $\approx 10^{-10}$. However, one should keep in mind that what is imaged in STM experiments is a constant LDOS surface at the STM *tip*'s position. This explains why also in the case of a bias voltage of 0.5 eV there is the same 1 order of magnitude difference between the corrugation of STM

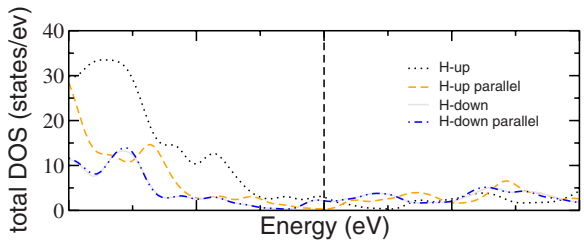

FIG. 7. (Color online) Total density of states (TDOS) calculated for the TPA-Cu(110) system in all four adsorption configurations considered in our study: (I) H-up, black dotted line; (II) H-up parallel, orange (gray) dashed line; (III) H-down, gray continuous line; and (IV) H-down parallel, blue (black) dotted-dashed line.

images obtained for a positive and negative applied bias voltage, respectively.

IV. SUMMARY

In this study, we have performed *ab initio* pseudopotential calculations in order to elucidate the role of the intermolecular interactions on the two-dimensional order of terephthalic acid (TPA) on Cu(110) surface. Since the chemical functionalization of this surface can be hindered by a hydrogen bond between TPA molecules, we have investigated if indeed this scenario takes place. Our calculations show that an adsorbate-substrate geometry with a hydrogen bond between adjacent TPA molecules is energetically not favorable. Instead, it relaxes to a geometry which exhibit a H—O bond in the carboxylic group plane oriented toward the benzene ring. The total energy of this adsorption configuration is slightly higher (≈0.08 eV) than that with a H—O bond pointing toward the vacuum interface (H-up geometry). This small energy difference opens the possibility that the hydrogen atom can fluctuate between these configurations. In consequence, we verified if such a process can take place by evaluating the energy barriers separating these geometries. Even if such a transition has a small rate at room temperature, it can be accelerated by applying a voltage via an STM tip like in a controlled nanomanipulation process. By calculating the lateral variation of the energy integrated LDOS, we have simulated the STM images for all TPA adsorption configurations under consideration to provide a connection to experiments. The simulated images exhibit specific features for each case considered, and thus it is possible to unambiguously identify in experiments which specific TPA-Cu(110) geometry is investigated. It is also important to note that for an applied bias voltage of ±0.5 eV, our simulations predict that only H-up and H-up parallel adsorption geometries can be imaged by STM.

ACKNOWLEDGMENT

The authors acknowledge financial support from the DFG Grant No. SPP 1243.

APPENDIX

In this appendix, we will shortly summarize the conditions for a chemical reaction of the vacuum exposed carboxylic acid group (—COOH), depending on the position of the hydrogen atom. Carboxylic acids are characterized by the presence of the carboxyl group, a functional group containing a hydroxyl unit (OH) attached to a carbonyl (CO) carbon as shown in Fig. 8(a). In a chemical language, this functional group is written as COOH or CO_2H. Much of the reactivity of the carboxylic acids can be anticipated if we see them as a hydroxyl-carbonyl derivate. The carbonyl part of a carboxylic acid is polarized in such a way that the hydrogen atom of the hydroxyl group and the carbon atom of the carbonyl groups carry a partial positive charge and the oxygen atoms possess a negative partial charge. Thus, the hydroxyl hydrogen is acidic and the oxygen atoms are basic with the carbonyl carbon (electrophilic center) being subjected to nucleophilic attack. The acidity and the basicity of the carboxylic acids are two properties that are strongly influenced by the interaction between the electron withdrawing carbonyl group and the hydroxy function.

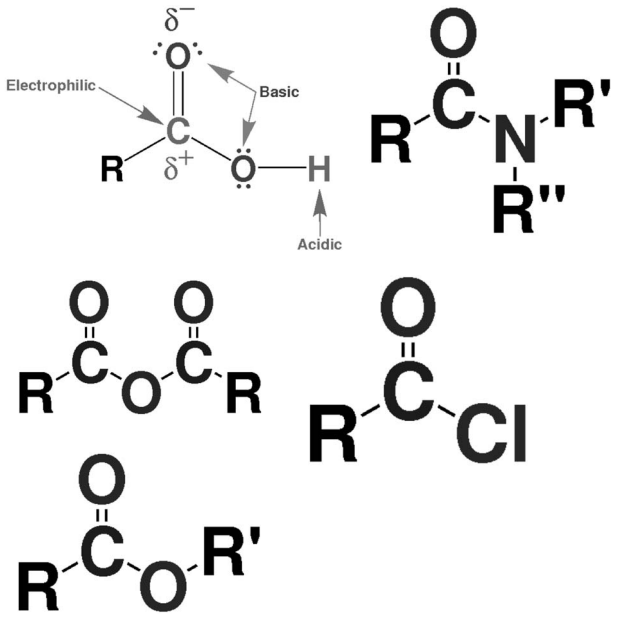

FIG. 8. The structure of some derivatives of carboxylic acids (R,R′,R″ represent a hydrogen atom or another organic radical). In (b) and (c), the acidic H is replaced by O═C—R and R′, respectively; in (d) and (e), the OH group is replaced by R″—N—R′ and Cl, respectively.

The reaction of a carboxylic acid with a metal cation or an organic cation (positive ion) occurs by replacing the proton in the COOH group. This results in a salt in case of a metal or of another organic molecule as carboxylic acid anhydride or an ester [Figs. 8(b) and 8(c)].[39,40] A replacement by other nucleophiles of the OH group of the carboxylic acids will result in molecules as acid chloride and amide [Figs. 8(d) and 8(e)].[39,40]

It is well established in organic chemistry[41,42] that in a qualitative description of a reaction between molecules, two basic conditions have to be fulfilled: (i) One requirement concerns the electronic part, i.e., the frontier orbitals have to meet specific condition for a bonding overlap. As two molecules collide, three major forces operate: (a) the occupied

orbitals of one repel the occupied orbitals of the other, (b) any positive charge on one attracts any negative charge of the other (and repels any positive), (c) the occupied orbitals (especially the highest occupied molecular orbitals) of each molecule interact with the unoccupied orbitals (especially the lowest unoccupied molecular orbitals) of the other, causing an attraction between the molecules. (ii) The second requirement is the steric interaction: when approaching one another, the molecules should have the proper configuration for a successful bonding interaction of the frontier orbitals (resulting in the formation of the new bonds).

In the case of terephthalic acid adsorbed on Cu(110) surface, one can easily imagine that depending on H position (up or down) of the carboxylic group exposed to the vacuum, a specific reaction can take place. In the case of the H-up configuration, the hydrogen atom will most probably hinder the reactions that can take place at the acidic H of the carboxylic group as well the nucleophilic attack at the carbonylic carbon. On the contrary, for the H-down configuration, there will be an easier access to the oxygen atom of the hydroxyl group (for replacing the H) or even to the carbon atom of the carbonyl group (for replacing the OH group).

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